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(54) Titre : COMPOSITION DE CRISTAUX LIQUIDES  
(54) Title: LIQUID-CRYSTALLINE COMPOSITION

(57) Abrégé/Abstract:

The invention relates to liquid crystalline substance mixtures which contain at least one compound selected from the group consisting of the compounds of the formula (Ia):  $Z^1-Y^1-A^1-Y^3-M^1-Y^4-A^2-Y^2-Z^2$  and of the formula (Ib):  $Z^3-Y^5-A^3-Y^7-M^2-P$ , wherein the variable P means hydrogen,  $C_1-C_{15}$ -alkyl or a  $-Y^8-A^4-Y^6-Z^4$  group,  $Z^1$  to  $Z^4$  polymerisable groups,  $Y^1$  to  $Y^8$  linking groups,  $A^1$  to  $A^4$  spacer and  $M^1$  and  $M^2$  mesogenic groups. Said liquid crystalline mixtures of substances optionally contain further additives selected from photoinitiators, reactive diluents and diluents, auxiliaries, colourants and stabilisers. The invention also relates to the use of such liquid crystalline mixtures of substances as printing ink, for printing or coating substrates, in electrooptic components, for forgery-proof marking of objects and for producing films or coatings.

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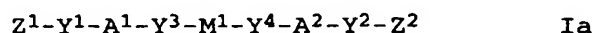
## Liquid-crystalline composition

### Abstract

5

The present invention relates to a liquid-crystalline composition which comprises, as components

- 10 A) a liquid-crystalline mixture comprising as least one compound selected from the group consisting of the compounds of the formula Ia



- 15 and of the formula Ib



- 20 where the variables, independently of one another, have the following meanings: P is hydrogen, C<sub>1</sub>-C<sub>15</sub>-alkyl or a -Y<sup>8</sup>-A<sup>4</sup>-Y<sup>6</sup>-Z<sup>4</sup> group, Z<sup>1</sup> to Z<sup>4</sup> are polymerizable groups, Y<sup>1</sup> to Y<sup>8</sup> are linking groups, A<sup>1</sup> to A<sup>4</sup> are spacers and M<sup>1</sup> and M<sup>2</sup> are mesogenic groups,

- 25 B) if desired, further additives selected from the group consisting of photoinitiators, reactive thinners and diluents,

- 30 C) if desired, further additives taken from the group consisting of antifoams and deaerators, lubricants and flow auxiliaries, thermally curing or radiation-curing auxiliaries, substrate wetting auxiliaries, wetting and dispersion auxiliaries, hydrophobicizing agents, adhesion promoters and auxiliaries for improving the scratch resistance,

35

- D) if desired, further additives selected from the group consisting of dyes and pigments, and

- 40 E) if desired, further additives selected from the group consisting of light, heat and/or oxidation stabilizers.

A detailed definition of the variables Z<sup>1</sup> to Z<sup>4</sup>, Y<sup>1</sup> to Y<sup>8</sup>, A<sup>1</sup> to A<sup>4</sup>, P, M<sup>1</sup> and M<sup>2</sup> is given in the description.

- 45 The present invention furthermore relates to the use of a liquid-crystalline composition of this type as a printing ink, for printing or coating substrates, in electro-optical

components, for counterfeiting-proof marking of articles and for the production of films or coatings which selectively reflect light in the wavelength range from 250 to 1300 nm, to a polymer or polymerized film obtained by polymerizing a liquid-crystalline composition according to the current invention and to the use of a polymerized film of this type as an optical filter, polarizer, decoration, counterfeiting-proof marking or reflection medium for the selective reflection of radiation in the wavelength range of 250 to 1300 nm, to a process for printing or coating the substrate using a liquid-crystalline composition according to the invention, and to substrates to which a liquid-crystalline composition according to the invention or a polymer or polymerized film according to the invention has been applied or which has been printed or coated by the process according to the invention.

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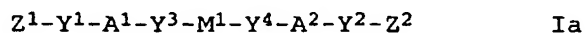
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Liquid-crystalline composition

The present invention relates to a liquid-crystalline composition  
5 which comprises, as components,

- A) a liquid-crystalline mixture comprising as least one compound  
selected from the group consisting of the compounds of the  
formula Ia

10



and of the formula Ib

15



where the variables, independently of one another, have the  
following meanings:

20

P is hydrogen, C<sub>1</sub>-C<sub>15</sub>-alkyl or a -Y<sup>8</sup>-A<sup>4</sup>-Y<sup>6</sup>-Z<sup>4</sup> group,

Z<sup>1</sup> to Z<sup>4</sup> are polymerizable groups,

Y<sup>1</sup> to Y<sup>8</sup> are linking groups,

25

A<sup>1</sup> to A<sup>4</sup> are spacers,

M<sup>1</sup> and M<sup>2</sup> are mesogenic groups,

- 30 B) if desired, further additives selected from the group  
consisting of

b1) photoinitiators,

35

b2) reactive thinners and

b3) diluents,

- 40 C) if desired, further additives taken from the group consisting  
of

c1) antifoams and deaerators,

c2) lubricants and flow auxiliaries

45

c3) thermally curing or radiation-curing auxiliaries,

- c4) substrate wetting auxiliaries,
- c5) wetting and dispersion auxiliaries,
- 5 c6) hydrophobicizing agents,
- c7) adhesion promoters and
- c8) auxiliaries for improving the scratch resistance,
- 10 D) if desired, further additives selected from the group consisting of
  - d1) dyes and
  - 15 d2) pigments
- and
- 20 E) if desired, further additives selected from the group consisting of light, heat and/or oxidation stabilizers.

A detailed definition of the variables  $Z^1$  to  $Z^4$ ,  $Y^1$  to  $Y^8$ ,  $A^1$  to  $A^4$ ,  $P$ ,  $M^1$  and  $M^2$  is given in the following description.

- 25 The present invention furthermore relates to the use of a liquid-crystalline composition of this type as a printing ink, for printing or coating substrates, in electro-optical components, for counterfeiting-proof marking of articles and for
- 30 the production of films or coatings which selectively reflect light in the wavelength range from 250 to 1300 nm.

- The present invention furthermore relates to a polymer or polymerized film obtained by polymerizing a liquid-crystalline
- 35 composition according to the current invention and to the use of a polymerized film of this type as an optical filter, polarizer, decoration, counterfeiting-proof marking or reflection medium for the selective reflection of radiation in the wavelength range of 250 to 1300 nm.

- 40 The present invention furthermore relates to a process for printing or coating the substrate using a liquid-crystalline composition according to the invention.

- 45 The present invention furthermore relates to substrates to which a liquid-crystalline composition according to the invention or a polymer or polymerized film according to the invention has been

applied or which has been printed or coated by the process according to the invention.

The specification WO 96/02597 describes a process for coating or printing substrates with a coating or printing composition which comprises said liquid-crystalline, polymerizable monomers. The coating or printing composition comprises either a chiral liquid-crystalline monomer or an achiral liquid-crystalline monomer and a non-liquid-crystalline compound, and polymeric binders and/or monomeric compounds which can be converted into the polymeric binder by polymerization.

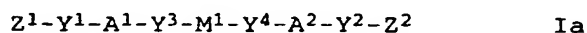
According to the examples given in this specification, these printing or coating compositions can be applied to various substrates by diverse application methods, for example by spraying or offset printing, where, after curing, for example by irradiation with UV light, they form strongly adhering layers which are resistant to external influences.

However, layers obtained in this way usually do not exhibit the desired degree of brilliance and brightness. Furthermore, the printing and coating compositions described are not ideally suitable for printing, in particular in screen printing, clonographic printing and letterpress printing, inter alia owing to their viscosity, which is without exception high.

It is an object of the present invention to provide a liquid-crystalline composition which can be used, inter alia, as a printing ink in common printing methods and enables the production of prints having high color fastness, brilliance and whiteness and the production of homogeneous and smooth liquid-crystalline layers and films.

We have found that this object is achieved by the liquid-crystalline composition described at the outset, which, in addition to the optional components B) to E), comprises, as component

A) a liquid-crystalline mixture comprising at least one compound selected from the group consisting of the compounds of the formula Ia



and of the formula Ib

4

 $Z^3-Y^5-A^3-Y^7-M^2-P$ 

Ib,

where the variables, independently of one another, have the following meanings:

5

$Z^1$  to  $Z^4$  are polymerizable groups,

$Y^1$  to  $Y^8$  are each a single chemical bond, oxygen, sulfur, -O-CO-, -CO-O-, -O-CO-O-, -CO-NR-, -NR-CO-,

10

-O-CO-NR-, -NR-CO-O- or -NR-CO-NR-,

R is hydrogen or  $C_1$ - $C_4$ -alkyl,

15

$A^1$  to  $A^4$  are spacers having 1 to 30 carbon atoms, in which the carbon chain may be interrupted by ether oxygen, thioether sulfur or by non-adjacent imino or  $C_1$ - $C_4$ -alkylimino groups.

20

P is hydrogen,  $C_1$ - $C_{15}$ -alkyl, which may be monosubstituted or polysubstituted by methyl, fluorine, chlorine or bromine and in which non-adjacent  $CH_2$ -groups may be replaced by oxygen, sulfur, -CO-, -O-CO-, -CO-O- or -O-CO-O-, or a  $-Y^8-A^4-Y^6-Z^4$  group, where the variables are as defined above,

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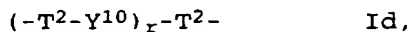
$M^1$  is a mesogenic group of the formula Ic



and

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$M^2$  is a mesogenic group of the formula Id



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where the variables in the formulae Ic and Id, independently of one another, are as defined below:

$T^1$ ,  $T^{1'}$  and  $T^2$  are divalent saturated or unsaturated carbocyclic or heterocyclic radicals,

40

$Y^9$  and  $Y^{10}$  are bridging units as defined for  $Y^1$  to  $Y^8$  or - $CH_2$ -O-, -O- $CH_2$ -, -CH=N-, -N=CH- or -N=N-,

r is a value of 0, 1, 2 or 3,

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where the radicals  $T^2$  and  $Y^{10}$ , in the case where r is not 0, may be identical or different.

## 5

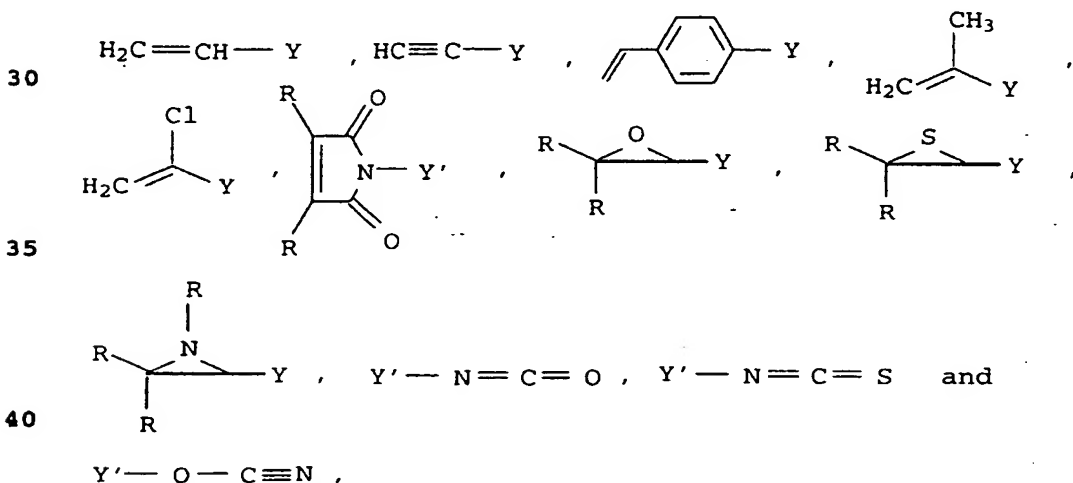
Component A) of the novel liquid-crystalline composition covers both liquid-crystalline mixtures which comprise pure liquid-crystalline compounds of the formulae Ia and/or Ib and mixtures which additionally include non-liquid-crystalline mixture constituents, but overall have liquid-crystalline behavior. These non-liquid-crystalline mixture constituents are usually byproducts formed during synthesis of liquid-crystalline compounds or during synthesis of mixtures of the liquid-crystalline compounds.

10

Besides the liquid-crystalline compounds of the formulae Ia and/or Ib (and the byproducts), component A) preferably also comprises at least one chiral compound, which, however, need not necessarily itself have liquid-crystalline behavior. The presence of such chiral compounds results - at least within certain temperature ranges - in the formation of chiral-nematic (cholesteric) phases, which usually have interesting optical properties.

20 However, it should be pointed out that, for the purposes of the present invention, the liquid-crystalline composition or the liquid-crystalline mixtures (component A)) need not necessarily include such chiral compounds.

25 Suitable polymerizable groups  $Z^1$  to  $Z^4$  are - in combination with the bridging units  $Y^1$  to  $Y^8$  - for example:



where Y is as defined for the bridging units  $Y^1$  to  $Y^8$ , i.e. a single chemical bond, oxygen, sulfur, -O-CO-, -CO-O-, -O-CO-O-, -CO-NR-, -NR-CO-, -O-CO-NR-, -NR-CO-O- or -NR-CO-NR-, and R is hydrogen or  $C_1$ - $C_4$ -alkyl, i.e. methyl, ethyl, n-propyl, i-propyl,



n-butyl, i-butyl, sec-butyl or tert-butyl, and Y' is a single chemical bond (hereinafter, the polymerizable groups Z<sup>1</sup> to Z<sup>4</sup> in combination with the bridging units Y<sup>1</sup> to Y<sup>8</sup> are referred to as polymerizable units or as Z-Y and/or Z-Y').

5

Of these polymerizable units, the cyanates can spontaneously trimerize to cyanurates. The maleimido group is particularly suitable for free-radical copolymerization with liquid-crystalline compounds of the formula Ia and/or Ib

10 containing styryl groups as polymerizable units.

Compounds of the formula Ia and/or Ib containing epoxide, thiirane, aziridine, isocyanate and isothiocyanate groups require further compounds containing complementary reactive units for

15 polymerization. Thus, for example, the corresponding isocyanates can be polymerized with alcohols to give urethanes and with amines to give urea derivatives. A similar situation applies to the corresponding thiiranes and aziridines.

20 The complementary reactive units may be present in the liquid-crystalline compounds, which are built up similarly to those of the formula Ia and/or Ib in component A) of liquid-crystalline composition. However, instead of the Z<sup>1</sup>-Y<sup>1</sup>-, Z<sup>2</sup>-Y<sup>2</sup>-, Z<sup>3</sup>-Y<sup>5</sup>- and/or Z<sup>4</sup>-Y<sup>6</sup>- groups, these compounds contain, for

25 example, hydroxyl, mercapto or NHR groups, where, in the latter, R is hydrogen or, for example, C<sub>1</sub>-C<sub>4</sub>-alkyl. The complementary reactive units may also be present in auxiliary compounds introduced into the liquid-crystalline composition.

30 Depending on whether component A) comprises liquid-crystalline compounds of the formula Ib containing one or two polymerizable units and, if it does, depending on the proportion of these compounds, and depending, inter alia, on the mixing ratio of liquid-crystalline compounds containing polymerizable units with

35 those containing complementary units or on the mixing ratio of liquid-crystalline compounds containing polymerizable units and auxiliary compounds containing complementary units, polymeric products are obtained with greatly different degrees of crosslinking, which are thus correspondingly matched to the

40 particular requirements.

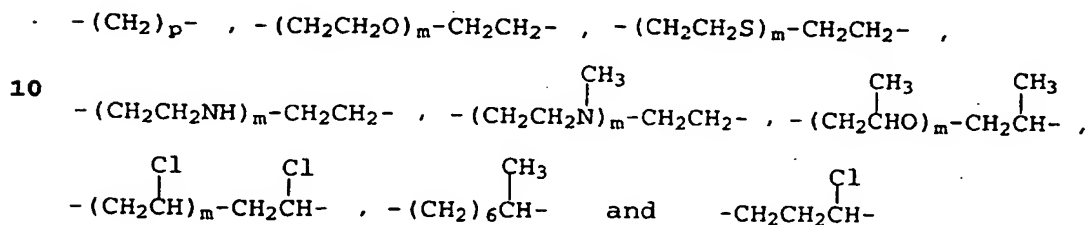
The spacers A<sup>1</sup> and A<sup>2</sup> usually contain from 1 to 30 carbon atoms, preferably from 1 to 12 carbon atoms, and consist of

predominantly linear aliphatic groups. The carbon chain may in

45 addition be monosubstituted or polysubstituted by methyl, fluorine, chlorine or bromine and/or interrupted by ether oxygen, thioether sulfur or by non-adjacent imino or C<sub>1</sub>-C<sub>4</sub>-alkylimino

groups. Suitable C<sub>1</sub>-C<sub>4</sub>-alkyl radicals for the latter are methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl and tert-butyl.

5 Examples of representative spacers are the following:



15

where

p is an integer from 1 to 30, preferably 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 or 12, and m is an integer from 1 to 14, preferably 1, 2 or 3.

20

Suitable C<sub>1</sub>-C<sub>15</sub>-alkyl radicals for P are preferably unbranched alkyl chains, for example methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl or n-pentadecyl.

25

These C<sub>1</sub>-C<sub>15</sub>-alkyl radicals may be monosubstituted or polysubstituted, generally up to trisubstituted, by methyl, fluorine, chlorine or bromine. P is then, for example, i-propyl ("1-methylethyl"), sec-butyl ("1-methylpropyl"), i-butyl

30 ("2-methylpropyl"), tert-butyl ("1,1-dimethylethyl"), 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,1-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl,

35 2,2-dimethylbutyl, 2,3-dimethylbutyl, 3,3-dimethylbutyl, 1,1,2-trimethylpropyl, 1,2,2-trimethylpropyl or the mono- di- or tri-methyl-substituted radicals n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl or n-pentadecyl and isomers thereof. Formal replacement of the  
40 methyl groups in the radicals mentioned by way of example by fluorine, chlorine or bromine gives the corresponding halogen-substituted C<sub>1</sub>-C<sub>15</sub>-alkyl radicals.

Non-adjacent CH<sub>2</sub> groups in C<sub>1</sub>-C<sub>15</sub>-alkyl may be replaced by oxygen,  
45 sulfur, -CO-, -O-CO-, -CO-O- or -O-CO-O-.

If this is the case, the CH<sub>2</sub> groups in the C<sub>1</sub>-C<sub>15</sub>-alkyl are preferably replaced by oxygen or sulfur.

If this is the case, up to four CH<sub>2</sub>-groups in the C<sub>1</sub>-C<sub>15</sub>-alkyl are preferably replaced.

Suitable C<sub>1</sub>-C<sub>15</sub>-alkyl radicals for P in which CH<sub>2</sub>-groups in the carbon chain have been replaced by ether oxygen are, for example,  
 2-methoxyethyl, 2-ethoxyethyl, 2-propoxyethyl, 2-butoxyethyl,  
 10 3-methoxypropyl, 3-ethoxypropyl, 3-butoxypropyl, 4-methoxybutyl,  
 4-ethoxybutyl, 4-butoxybutyl, 3,6-dioxaheptyl, 3,6-dioxaoctyl,  
 4,8-dioxanonyl, 3,7-dioxaoctyl, 3,7-dioxanonyl, 4,7-dioxaoctyl,  
 4,7-dioxanonyl, 4,8-dioxadecyl, 3,6,8-trioxadecyl,  
 3,6,9-trioxaundecyl, 3,6,9,12-tetraoxatridecyl and  
 15 3,6,9,12-tetraoxatetradecyl, and the corresponding sulfur  
 analogs.

P can also be a -Y<sup>8</sup>-A<sup>4</sup>-Y<sup>6</sup>-Z<sup>4</sup> group, in which the variables are as defined above.

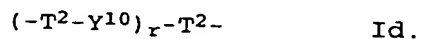
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M<sup>1</sup> corresponds to a mesogenic group of the formula Ic



25 and

M<sup>2</sup> corresponds to a mesogenic group of the formula Id



30

In the formulae Ic and Id, the variables, independently of one another, are as defined below:

T<sup>1</sup>, T<sup>1'</sup> and T<sup>2</sup> are divalent saturated or unsaturated carbocyclic  
 35 or heterocyclic radicals,

Y<sup>9</sup> and Y<sup>10</sup> are bridging units as defined for Y<sup>1</sup> to Y<sup>8</sup> or -CH<sub>2</sub>-O-,  
 -O-CH<sub>2</sub>-, -CH=N-, -N=CH- or -N=N- and

40 r is 0, 1, 2 or 3.

In the case where r is 1, 2 or 3, the radicals T<sup>2</sup> and Y<sup>10</sup> may be identical or different.

45 r is preferably 1 or 2.

## 26

Disperbyk®-167, Disperbyk®-170, Disperbyk®-174, Disperbyk®-180, Disperbyk®-181, Disperbyk®-182, Disperbyk®-183, Disperbyk®-184, Disperbyk®-185, Disperbyk®-190, Anti-Terra®-U, Anti-Terra®-U 80, Anti-Terra®-P, Anti-Terra®-203, Anti-Terra®-204, Anti-Terra®-  
 5 206, BYK®-151, BYK®-154, BYK®-155, BYK®-P 104 S, BYK®-P 105, Lactimon®, Lactimon®-WS and Bykumen® .

The amount of the auxiliaries in group c5) used depends principally on the pigment surface area to be coated and on the  
 10 mean molecular weight of the auxiliary.

For inorganic pigments and low-molecular-weight auxiliaries, a proportion of the latter of from about 0.5 to 2.0% by weight, based on the total weight of pigment and auxiliary, is usually  
 15 expected. In the case of high-molecular-weight auxiliaries, the proportion increases to from about 1.0 to 30% by weight.

In the case of organic pigments and low-molecular-weight auxiliaries, the proportion of the latter is from about 1.0 to  
 20 5.0% by weight, based on the total weight of pigment and auxiliary. In the case of high-molecular-weight auxiliaries, this proportion can be between about 10.0 and 90% by weight.

In any case, a preliminary experiment is therefore advisable, but  
 25 this can be accomplished simply by the person skilled in the art.

The hydrophobicizing agents in group c6) can be used to give water-repellent properties to prints or coatings produced, for example, using compositions according to the invention. This  
 30 prevents or at least greatly suppresses swelling due to water absorption and thus a change in, for example, the optical properties of such prints or coatings. In addition, when the composition is used, for example, as a printing ink in offset printing, water absorption can thereby be prevented or at least  
 35 greatly reduced.

Such hydrophobicizing agents are commercially available, for example, from Tego as Tego® Phobe WF, Tego® Phobe 1000, Tego® Phobe 1000 S, Tego® Phobe 1010, Tego® Phobe 1030, Tego® Phobe  
 40 1010, Tego® Phobe 1010, Tego® Phobe 1030, Tego® Phobe 1040, Tego® Phobe 1050, Tego® Phobe 1200, Tego® Phobe 1300, Tego® Phobe 1310 and Tego® Phobe 1400.

The auxiliaries in group c6) are usually employed in a proportion  
 45 of from about 0.05 to 5.0% by weight, preferably from about 0.1 to 3.0% by weight, based on the total weight of the liquid-crystalline composition.

Adhesion promoters from group c7) serve to improve the adhesion of two interfaces in contact. It is directly evident from this that essentially the only fraction of the adhesion promoter that  
5 is effective is that located at one or the other or at both interfaces. If, for example, it is desired to apply liquid or pasty printing inks, coating compositions or paints to a solid substrate, this generally means that the adhesion promoter must be added directly to the latter or the substrate must be  
10 pretreated with the adhesion promoters (also known as priming), i.e. this substrate is given modified chemical and/or physical surface properties.

If the substrate has previously been primed with a primer, this  
15 means that the interfaces in contact are that of the primer on the one hand and of the printing ink or coating composition or paint on the other hand. In this case, not only the adhesion properties between the substrate and the primer, but also between the substrate and the printing ink or coating composition or  
20 paint play a part in adhesion of the overall multilayer structure on the substrate.

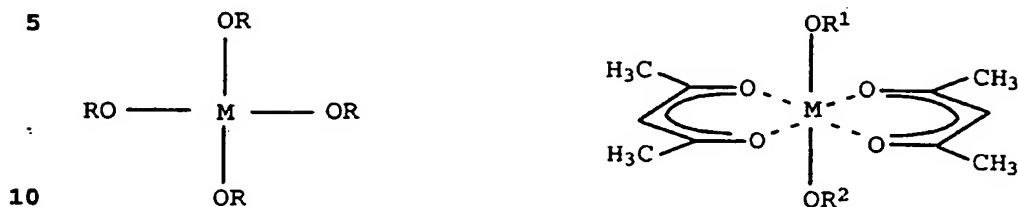
Adhesion promoters in the broader sense which may be mentioned are also the substrate wetting auxiliaries already listed under  
25 group c4), but these generally do not have the same adhesion promotion capacity.

In view of the widely varying physical and chemical natures of substrates and of printing inks, coating compositions and paints  
30 intended, for example, for their printing or coating, the multiplicity of adhesion promoter systems is not surprising.

Adhesion promoters based on silanes are, for example,  
3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane,  
35 3-aminopropylmethyldiethoxysilane,  
N-aminoethyl-3-aminopropyltrimethoxysilane,  
N-aminoethyl-3-aminopropylmethyldimethoxysilane,  
N-methyl-3-aminopropyltrimethoxysilane,  
3-ureidopropyltriethoxysilane,  
40 3-methacryloyloxypropyltrimethoxysilane,  
3-glycidyloxypropyltrimethoxysilane,  
3-mercaptopropyltrimethoxysilane, 3-chloropropyltrimethoxysilane  
and vinyltrimethoxysilane. These and other silanes are  
commercially available from Hüls, for example under the tradename  
45 DYNASILAN®.

Adhesion promoters based on titanates/zirconates and titanium

zirconium bisacetylacetonates conform, for example, to the following formulae:



in which M is titanium or zirconium, and R, R<sup>1</sup> and R<sup>2</sup> are C<sub>1</sub>-C<sub>4</sub>-alkyl, for example i-propyl or n-butyl. Examples of such compounds are tetra-i-propyl titanate, tetra-n-butyl titanate, titanium bis(acetylacetonate) diisopropoxide, titanium bis(acetylacetonate) dibutoxide, titanium bis(acetylacetonate) monobutoxide monoisopropoxide and titanium bis(acetylacetonate) monoethoxide monoisopropoxide.

20 Other titanium and zirconium compounds which can be used as adhesion promoters are n-butyl polytitanate, isopropyl triisostearoyl titanate, isopropyl tris(N-ethylaminoethylamino) titanate and zirconium bis(diethyl citrate) diisopropoxide.

25 These and other titanium and zirconium compounds are available, for example, under the tradenames TYZOR<sup>®</sup> (DuPont), Ken-React<sup>®</sup> (Kenrich Petrochemicals Inc.) and Tilcom<sup>®</sup> (Tioxide Chemicals).

Zirconium aluminates, as available, for example, under the tradename Manchem<sup>®</sup> (Rhône Poulenc), can also serve as adhesion promoters.

Other compounds which are suitable, for example, as adhesion-promoting additives in printing inks or paints are chlorinated polyolefins (available, for example, from Eastman Chemical and Toyo Kasei), polyesters (available, for example, from Hüls AG, BASF Aktiengesellschaft, Gebr. Borchers AG, Pluess-Stauffer AG, Hoechst AG and Worlee), compounds based on sucrose, for example sucrose benzoate and sucrose acetoisobutyrate (the latter available, for example, from Eastman Chemical), phosphoric acid esters (available, for example, from The Lubrizol Company and Hoechst AG) and polyethyleneimines (available, for example, from BASF Aktiengesellschaft), and compounds which are suitable, for example, as adhesion-promoting additives in printing inks for flexographic, film and packaging

## 29

printing, colophonium ester (available, for example, from Robert Kraemer GmbH).

The usual procedure is, for example, appropriately to pre-treat  
5 the substrate to be printed or coated, i.e. to use such additives as primers.

Corresponding technical information from the manufacturers of such additives should generally be used or the person skilled in  
10 the art can obtain this information in a simple manner through corresponding preliminary experiments.

However, if these additives are to be added as auxiliaries from group c7) to the compositions according to the invention, their  
15 proportion usually corresponds to from about 0.05 to 5.0% by weight, based on the total weight of the liquid-crystalline composition. These concentration data serve merely as guidance, since the amount and identity of the additive are determined in each individual case by the nature of the substrate and of the  
20 printing/coating composition. Corresponding technical information is usually available from the manufacturers of such additives for this case or can be determined in a simple manner by the person skilled in the art through corresponding preliminary experiments.

25 The auxiliaries for improving the scratch resistance in group c8) include, for example, the abovementioned products TEGO® Rad 2100, TEGO® Rad 2200, TEGO® Rad 2500, TEGO® Rad 2600 and TEGO® Rad 2700, which are available from Tego.

30 For these auxiliaries, the amount data given for group c3) are likewise suitable, i.e. these additives are usually employed in a proportion of from about 0.1 to 5.0% by weight, preferably from about 0.1 to 3.0% by weight, based on the total weight of the liquid-crystalline composition.

35

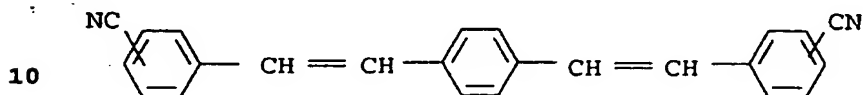
The dyes in group d1) include, for example, dyes from the class of the monoazo dyes, isoindoline derivatives, derivatives of naphthalene- or perylenetetracarboxylic acid, thioindigo derivatives, azomethine derivatives, quinacridones, dioxazines,  
40 pyrazoloquinazolones and basic dyes, such as triarylmethane dyes and their salts.

It is also possible, in particular, to add photochromic, thermochromic or luminescent dyes and dyes which have a  
45 combination of these properties to the compositions according to

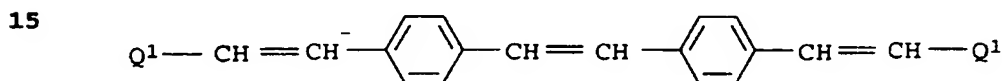
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the invention. Besides typical fluorescent dyes, the term fluorescent dyes is also taken to mean optical brighteners.

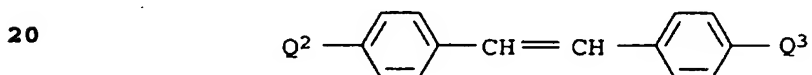
The latter belong, for example, to the class of the bisstyrylbenzenes, in particular the cyanostyryl compounds, and conform to the formula



Further suitable optical brighteners from the class of the stilbenes have, for example, the formulae



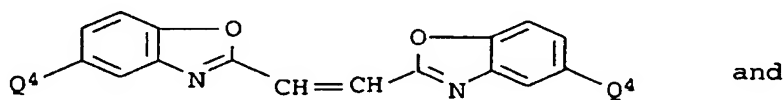
and



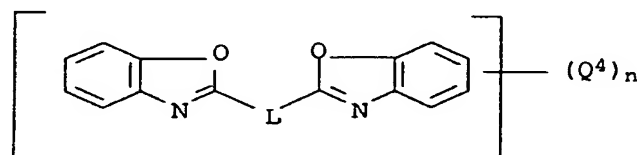
in which Q<sup>1</sup> is in each case C<sub>1</sub>-C<sub>4</sub>-alkoxycarbonyl or cyano, Q<sup>2</sup> is benzoxazol-2-yl, which may be monosubstituted or disubstituted by C<sub>1</sub>-C<sub>4</sub>-alkyl, in particular methyl, Q<sup>3</sup> is C<sub>1</sub>-C<sub>4</sub>-alkoxycarbonyl or 3-(C<sub>1</sub>-C<sub>4</sub>-alkyl)-1,2,4-oxadiazol-3-yl.

Further suitable optical brighteners from the class of the benzoxazoles conform, for example, to the formulae

30



35



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in which Q<sup>4</sup> is in each case C<sub>1</sub>-C<sub>4</sub>-alkyl, in particular methyl, L is a radical of the formula

45



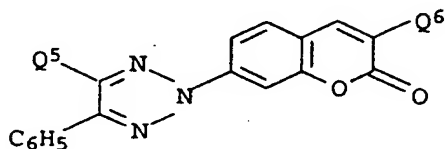


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and n is an integer from 0 to 2.

Suitable optical brighteners from the class of the coumarines have, for example, the formula

5



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where

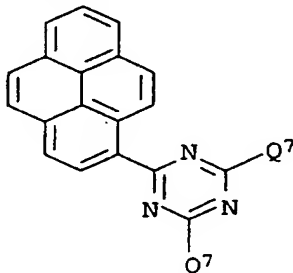
Q<sup>5</sup> is C<sub>1</sub>-C<sub>4</sub>-alkyl, and

15

Q<sup>6</sup> is phenyl or 3-halopyrazol-1-yl, in particular 3-chloropyrazol-1-yl.

Further suitable optical brighteners from the class of the pyrenes conform, for example, to the formula

25



30 where

Q<sup>7</sup> is in each case C<sub>1</sub>-C<sub>4</sub>-alkoxy, in particular methoxy.

The abovementioned brighteners can be used either alone or in mixtures with one another.

The abovementioned optical brighteners are generally known and commercially available products. They are described, for example, in Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition, Volume A18, pages 156 to 161, or can be obtained by the methods given therein.

In particular, use is made, if this is desired, of one or more optical brighteners from the class of the bisstyrylbenzenes, in particular the cyanostyrylbenzenes.

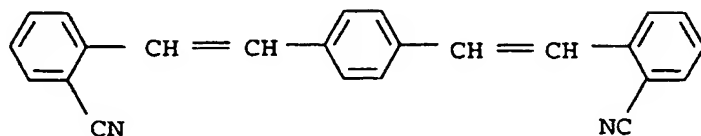
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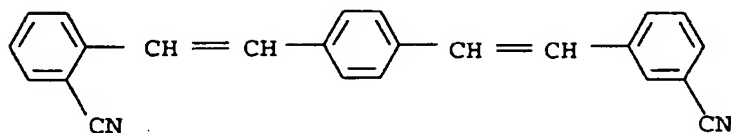
The latter can be used as individual compounds, but also as a mixture of the isomeric compounds.

The isomers conform to the formulae

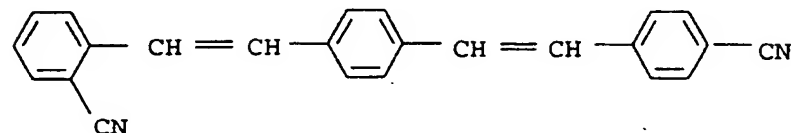
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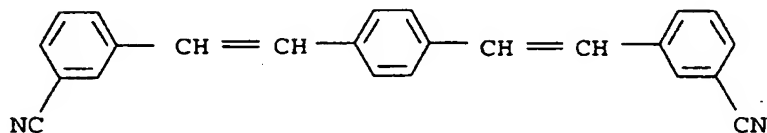
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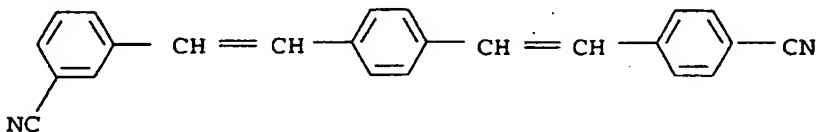
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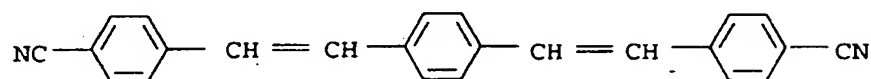
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Optical brighteners are marketed commercially, for example, as Ultraphor<sup>®</sup> SF 004, Ultraphor<sup>®</sup> SF MO, Ultraphor<sup>®</sup> SF MP and Ultraphor<sup>®</sup> SF PO by BASF.

40

Suitable fluorescent dyes are, for example, perylene derivatives described in DE-A 32 35 526, DE-A 34 00 991, DE-A 34 34 059 and DE-A 35 45 004, European Patent Application 0 033 079 and European Patent 0 055 363.

45

## 33

Fluorescent dyes are marketed, for example, as Lumogen® Yellow 083, Lumogen® Orange 240, Lumogen® Red 300, Lumogen® Violet 570 and Thermoplast® F Yellow 084 by BASF.

- 5 The pigments in group d2) include both inorganic and organic pigments. An overview of inorganic colored pigments which can be used in compositions according to the invention is given by the book by H. Endriß "Aktuelle anorganische Bunt-Pigmente" (Editor U. Zorll, Curt-R.-Vincentz-Verlag Hannover (1997)). In addition,  
10 further pigments not listed in the abovementioned book are Pigment Black 6 and Pigment Black 7 (carbon black), Pigment Black 11 (iron oxide black,  $\text{Fe}_3\text{O}_4$ ), Pigment White 4 (zinc oxide,  $\text{ZnO}$ ), Pigment White 5 (Lithopone,  $\text{ZnS}/\text{BaSO}_4$ ), Pigment White 6 (titanium oxide,  $\text{TiO}_2$ ) and Pigment White 7 (zinc sulfide  $\text{ZnS}$ ).

- 15 An overview of organic pigments which can be added to the compositions according to the invention is given by the book by W. Herbst and K. Hunger "Industrielle organische Pigmente - Herstellung, Eigenschaften, Anwendung" (VCH-Verlag Weinheim, New  
20 York, Basle, Cambridge, Tokyo, second edition (1995)).

It is also possible to add magnetic, electroconductive, photochromic, thermochromic or luminescent pigments and pigments which have a combination of these properties to the compositions  
25 according to the invention.

- Besides some organic pigments, for example Lumogen® Yellow 0790 (BASF Aktiengesellschaft), suitable pigments having luminescent properties are also inorganic, doped or undoped compounds  
30 essentially based on alkaline earth metal oxides, alkaline earth metal transition metal oxides, alkaline earth metal/aluminum oxides, alkaline earth metal/silicon oxides or alkaline earth metal/phosphorus oxides, alkaline earth metal halides, Zn/silicon oxides, Zn/alkaline earth metal halides; rare-earth metal oxides,  
35 rare-earth metal/transition metal oxides, rare-earth metal aluminum oxides, rare-earth metal/silicon oxides or rare-earth metal/phosphorus oxides, rare-earth metal oxide sulfides or oxide halides, zinc oxide, sulfide or selenide, cadmium oxide, sulfide or selenide or zinc/cadmium oxide, sulfide or selenide, where the  
40 cadmium-containing compounds are of lower importance owing to their toxicological and ecological relevance.

- The dopants used in these compounds are usually aluminum, tin, antimony, rare-earth metals, such as cerium, europium or terbium,  
45 transition metals, such as manganese, copper, silver or zinc, or combinations of these elements.

## 34

The following luminescent pigments are given by way of example, the notation "compound:element(s)" being taken to mean to the relevant person skilled in the art that said compound has been doped with the corresponding element(s). In addition, for  
 5 example, the notation "(P,V)", denotes that the corresponding lattice positions in the solid structure of the pigment are randomly occupied by phosphorus and vanadium.

Examples of such compounds which are capable of luminescence are  
 10  $\text{MgWO}_4$ ,  $\text{CaWO}_4$ ,  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}$ ,  $\text{BaMg}_2\text{Al}_{10}\text{O}_{27}:\text{Eu}$ ,  $\text{MgAl}_{11}\text{O}_{19}:\text{Ce,Tb}$ ,  
 $\text{MgSiO}_3:\text{Mn}$ ,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{F,Cl}):\text{Sb,Mn}$ ,  $(\text{SrMg})_2\text{P}_2\text{O}_7:\text{Eu}$ ,  $\text{SrMg}_2\text{P}_2\text{O}_7:\text{Sn}$ ,  
 $\text{BaFCl}:\text{Eu}$ ,  $\text{Zn}_2\text{SiO}_4:\text{Mn}$ ,  $(\text{Zn,Mg})\text{F}_2:\text{Mn}$ ,  $\text{Y}_2\text{O}_3:\text{Eu}$ ,  $\text{YVO}_4:\text{Eu}$ ,  $\text{Y(P,V)O}_4:\text{Eu}$ ,  
 $\text{Y}_2\text{SiO}_5:\text{Ce,Tb}$ ,  $\text{Y}_2\text{O}_2\text{S}:\text{Eu}$ ,  $\text{Y}_2\text{O}_2\text{S}:\text{Tb}$ ,  $\text{La}_2\text{O}_2\text{S}:\text{Tb}$ ,  $\text{Gd}_2\text{O}_2\text{S}:\text{Tb}$ ,  $\text{LaOBr}:\text{Tb}$ ,  
 15  $\text{ZnO}:\text{Zn}$ ,  $\text{ZnS}:\text{Mn}$ ,  $\text{ZnS}:\text{Ag}$ ,  $\text{ZnS/CdS}:\text{Ag}$ ,  $\text{ZnS}:\text{Cu,Al}$ ,  $\text{ZnSe}:\text{Mn}$ ,  $\text{ZnSe}:\text{Ag}$   
 and  $\text{ZnSe}:\text{Cu}$ .

Examples which may be mentioned of light, heat and/or oxidation stabilizers as component E) are the following:

- 20 alkylated monophenols, such as 2,6-di-tert-butyl-4-methylphenol,  
 2-tert-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-ethylphenol,  
 2,6-di-tert-butyl-4-n-butylphenol,  
 2,6-di-tert-butyl-4-isobutylphenol,  
 2,6-dicyclopentyl-4-methylphenol,
- 25 2-( $\alpha$ -methylcyclohexyl)-4,6-dimethylphenol,  
 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol,  
 2,6-di-tert-butyl-4-methoxymethylphenol, nonylphenols which have  
 a linear or branched side chain, for example  
 2,6-dinonyl-4-methylphenol,
- 30 2,4-dimethyl-6-(1'-methylundec-1'-yl)phenol,  
 2,4-dimethyl-6-(1'-methylheptadec-1'-yl)phenol,  
 2,4-dimethyl-6-(1'-methyltridec-1'-yl)phenol and mixtures of  
 these compounds,  
 alkylthiomethylphenols, such as
- 35 2,4-dioctylthiomethyl-6-tert-butylphenol,  
 2,4-dioctylthiomethyl-6-methylphenol,  
 2,4-dioctylthiomethyl-6-ethylphenol and  
 2,6-didodecylthiomethyl-4-nonylphenol,
- 40 Hydroquinones and alkylated hydroquinones, such as  
 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butylhydroquinone,  
 2,5-di-tert-amylhydroquinone, 2,6-diphenyl-4-octadecyloxyphenol,  
 2,6-di-tert-butylhydroquinone,  
 2,5-di-tert-butyl-4-hydroxyanisole,
- 45 3,5-di-tert-butyl-4-hydroxyanisole,

## 35

3,5-di-tert-butyl-4-hydroxyphenyl stearate and  
bis(3,5-di-tert-butyl-4-hydroxyphenyl)adipate,

Tocopherols, such as  $\alpha$ -tocopherol,  $\beta$ -tocopherol,  $\gamma$ -tocopherol,  
5  $\delta$ -tocopherol and mixtures of these compounds, and tocopherol  
derivatives, such as tocopheryl acetate, succinate, nicotinate  
and polyoxyethylenesuccinate ("tocofersolate"),

hydroxylated diphenyl thioethers, such as  
10 2,2'-thiobis(6-tert-butyl-4-methylphenol),  
2,2'-thiobis(4-octylphenol),  
4,4'-thiobis(6-tert-butyl-3-methylphenol),  
4,4'-thiobis(6-tert-butyl-2-methylphenol),  
4,4'-thiobis(3,6-di-sec-amylphenol) and  
15 4,4'-bis(2,6-dimethyl-4-hydroxyphenyl) disulfide,

Alkylidenebisphenols, such as  
2,2'-methylenebis(6-tert-butyl-4-methylphenol),  
2,2'-methylenebis(6-tert-butyl-4-ethylphenol),  
20 2,2'-methylenebis[4-methyl-6-( $\alpha$ -methylcyclohexyl)phenol],  
2,2'-methylenebis(4-methyl-6-cyclohexylphenol),  
2,2'-methylenebis(6-nonyl-4-methylphenol),  
2,2'-methylenebis(4,6-di-tert-butylphenol),  
2,2'-ethylenidenebis(4,6-di-tert-butylphenol),  
25 2,2'-ethylenidenebis(6-tert-butyl-4-isobutylphenol),  
2,2'-methylenebis[6-( $\alpha$ -methylbenzyl)-4-nonylphenol],  
2,2'-methylenebis[6-( $\alpha,\alpha$ -dimethylbenzyl)-4-nonylphenol],  
4,4'-methylenebis(2,6-di-tert-butylphenol),  
4,4'-methylenebis(6-tert-butyl-2-methylphenol),  
30 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)butane,  
2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol,  
1,1,3-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)butane,  
1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecyl-  
mercaptobutane, ethylene glycol  
35 bis[3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)butyrate],  
bis(3-tert-butyl-4-hydroxy-5-methylphenyl)dicyclopentadiene,  
bis[2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-  
methylphenyl] terephthalate,  
1,1-bis(3,5-dimethyl-2-hydroxyphenyl)butane,  
40 2,2-bis(3,5-di-tert-butyl-4-hydroxyphenyl)propane,  
2,2-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-4-n-dodecyl-  
mercaptobutane and  
1,1,5,5-tetrakis(5-tert-butyl-4-hydroxy-2-methylphenyl)pentane,  
45 O-, N- and S-benzyl compounds, such as  
3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxydibenzyl ether,  
octadecyl 4-hydroxy-3,5-dimethylbenzylmercaptoacetate, tridecyl

## 36

- 4-hydroxy-3,5-di-tert-butylbenzylmercaptoacetate,  
 tris(3,5-di-tert-butyl-4-hydroxybenzyl)amine,  
 bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)  
 dithioterephthalate, bis(3,5-di-tert-butyl-4-hydroxybenzyl)  
 5 sulfide and isooctyl-3,5-  
 di-tert-butyl-4-hydroxybenzylmercaptoacetate,  
 aromatic hydroxybenzyl compounds, such as  
 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethyl-  
 10 benzene,  
 1,4-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-2,3,5,6-tetramethyl-  
 benzene and 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)phenol,  
 Triazine compounds, such as  
 15 2,4-bis(octylmercapto)-6-(3,5-di-tert-butyl-4-hydroxyanilino)-  
 1,3,5-triazine,  
 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5  
 -triazine,  
 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,3,5  
 20 -triazine,  
 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,2,3-triazine,  
 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl) isocyanurate,  
 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)  
 isocyanurate,  
 25 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenylethyl)-1,3,5-  
 triazine,  
 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexahydro-  
 1,3,5-triazine, 1,3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl)  
 isocyanurate and 1,3,5-tris(2-hydroxyethyl) isocyanurate,  
 30 Benzylphosphonates, such as dimethyl  
 2,5-di-tert-butyl-4-hydroxybenzylphosphonate, diethyl  
 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl  
 3,5-di-tert-butyl-4-hydroxybenzylphosphonate and dioctadecyl  
 35 5-tert-butyl-4-hydroxy-3-methylbenzylphosphonate,  
 Acylaminophenols, such as 4-hydroxylauroylanilide,  
 4-hydroxystearoylanilide and octyl  
 N-(3,5-di-tert-butyl-4-hydroxyphenyl)carbamate,  
 40 Propionic and acetic esters, for example of monohydric or  
 polyhydric alcohols, such as methanol, ethanol, n-octanol,  
 i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene  
 glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol,  
 45 diethylene glycol, triethylene glycol, pentaerythritol,  
 tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxalamide,  
 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol,

trimethylolpropane and  
4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]-octane,

Propionamides based on amine derivatives, such as

- 5 N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylene diamine,  
N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylene-  
diamine and  
N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine,
- 10 Ascorbic acid (Vitamin C) and ascorbic acid derivatives, such as  
ascorbyl palmitate, laurate and stearate, and ascorbyl sulfate  
and phosphate,
- 15 Antioxidants based on amine compounds, such as  
N,N'-diisopropyl-p-phenylenediamine,  
N,N'-di-sec-butyl-p-phenylenediamine,  
N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine,  
N,N'-bis(1-ethyl-3-methylpentyl)-p-phenylenediamine,
- 20 N,N'-bis(1-methylheptyl)-p-phenylenediamine,  
N,N'-dicyclohexyl-p-phenylenediamine,  
N,N'-diphenyl-p-phenylenediamine,  
N,N'-bis(2-naphthyl)-p-phenylenediamine,  
N-isopropyl-N'-phenyl-p-phenylenediamine,
- 25 N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine,  
N-(1-methylheptyl)-N'-phenyl-p-phenylenediamine,  
N-cyclohexyl-N'-phenyl-p-phenylenediamine,  
4-(p-toluenesulfamoyl)diphenylamine,  
N,N'-dimethyl-N,N'-di-sec-butyl-p-phenylenediamine,
- 30 diphenylamine, N-allyldiphenylamine, 4-isopropoxydiphenylamine,  
N-phenyl-1-naphthylamine, N-(4-tert-octylphenyl)-1-naphthylamine,  
N-phenyl-2-naphthylamine, octyl-substituted diphenylamine, such  
as p,p'-di-tert-octyldiphenylamine, 4-n-butylaminophenol,  
4-butyrylaminophenol, 4-nonanoylaminophenol,
- 35 4-dodecanoylaminophenol, 4-octadecanoylaminophenol,  
bis[4-methoxyphenyl]amine,  
2,6-di-tert-butyl-4-dimethylaminomethylphenol,  
2,4-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane,  
N,N,N',N'-tetramethyl-4,4'-diaminodiphenylmethane,
- 40 1,2-bis[(2-methylphenyl)amino]ethane,  
1,2-bis(phenylamino)propane, (o-tolyl)biguanide,  
bis[4-(1',3'-dimethylbutyl)phenyl]amine, tert-octyl-substituted  
N-phenyl-1-naphthylamine, a mixture of mono- and dialkylated  
tert-butyl/tert-octyldiphenylamine, a mixture of mono- and
- 45 dialkylated nonyldiphenylamine, a mixture of mono- and  
dialkylated dodecyldiphenylamine, a mixture of mono- and  
dialkylated isopropyl/isohexyldiphenylamine, a mixture of mono-

- and dialkylated tert-butyldiphenylamine, 2,3-dihydro-3,3-dimethyl-4H-1,4-benzothiazine, phenothiazine, a mixture of mono- and dialkylated tert-butyl/tert-octylphenothiazine, a mixture of mono- and dialkylated tert-octylphenothiazine,
- 5 N-allylphenothiazine, N,N,N',N'-tetraphenyl-1,4-diaminobut-2-ene, N,N-bis(2,2,6,6-tetramethylpiperidin-4-yl)hexamethylenediamine, bis(2,2,6,6-tetramethylpiperidin-4-yl) sebacate, 2,2,6,6-tetramethylpiperidin-4-one and 2,2,6,6-tetramethylpiperidin-4-ol,
- 10 Phosphites and phosphonites, such as triphenylphosphite, diphenyl alkyl phosphite, phenyl dialkyl phosphite, tris(nonylphenyl) phosphite, trilauryl phosphite, trioctadecyl phosphite, distearyl pentaerythritol diphosphite, tris(2,4-di-tert-butylphenyl) phosphite, diisodecyl pentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl) pentaerythritol diphosphite, diisodecyloxy pentaerythritol diphosphite, bis(2,4-di-tert-butyl-6-methylphenyl) pentaerythritol
- 20 diphosphite, bis(2,4,6-tris(tert-butylphenyl)) pentaerythritol diphosphite, tristearyl sorbitol triphosphite, tetrakis(2,4-di-tert-butylphenyl) 4,4'-biphenylenediphosphonite, 6-isooctyloxy-2,4,8,10-tetra-tert-butyl-12H-dibenz[d,g]-1,3,2-dioxaphosphocine,
- 25 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyl-dibenz[d,g]-1,3,2-dioxaphosphocine, bis(2,4-di-tert-butyl-6-methylphenyl) methyl phosphite and bis(2,4-di-tert-butyl-6-methylphenyl) ethyl phosphite,
- 30 2-(2'-Hydroxyphenyl)benzotriazoles, such as 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-5'-(1,1,3,3-tetramethylbutyl)phenyl)benzotriazole,
- 35 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-methylphenyl)-5-chlorobenzotriazole, 2-(3'-sec-butyl-5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-4'-octyloxyphenyl)benzotriazole,
- 40 2-(3',5'-di-tert-amyl-2'-hydroxyphenyl)benzotriazole, 2-(3',5'-bis-( $\alpha$ , $\alpha$ -dimethylbenzyl)-2'-hydroxyphenyl)benzotriazole, a mixture of 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonyl)ethyl)phenyl)-5-chlorobenzotriazole,
- 45 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonyl]ethyl)-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonyl)ethyl)phenyl)-5-



- chlorobenzotriazole,  
 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonylethyl)phenyl)-  
 benzotriazole,  
 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonylethyl)phenyl)-  
 5 benzotriazole,  
 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonylethyl]-2'-hydroxy  
 phenyl)benzotriazole,  
 2-(3'-dodecyl-2'-hydroxy-5'-methylphenyl)benzotriazole and  
 2-(3'-tert-butyl-2'-hydroxy-5'-(2-isooctyloxycarbonylethyl)phenyl  
 10 benzotriazole,  
 2,2'-methylenebis[4-(1,1,3,3-tetramethylbutyl)-6-benzotriazol-2-  
 ylphenol]; the product of complete esterification of  
 2-[3'-tert-butyl-5'-(2-methoxycarbonylethyl)-2'-hydroxyphenyl]-2H  
 -benzotriazole with polyethylene glycol 300;  
 15 [R-CH<sub>2</sub>CH<sub>2</sub>-COO(CH<sub>2</sub>)<sub>3</sub>]<sub>2</sub>, where R =  
 3'-tert-butyl-4'-hydroxy-5'-2H-benzotriazol-2-ylphenyl],  
 sulfur-containing peroxide scavengers and sulfur-containing  
 antioxidants, such as esters of 3,3'-thiodipropionic acid, for  
 20 example the lauryl, stearyl, myristyl and tridecyl esters,  
 mercaptobenzimidazole and the zinc salt of  
 2-mercaptobenzimidazole, dibutylzinc dithiocarbamates,  
 dioctadecyl disulfide and pentaerythritol  
 tetrakis(β-dodecylmercapto)propionate,  
 25 2-hydroxybenzophenones, such as the 4-hydroxy, 4-methoxy,  
 4-octyloxy, 4-decyloxy, 4-dodecyloxy, 4-benzyloxy,  
 4,2',4'-trihydroxy and 2'-hydroxy-4,4'-dimethoxy derivatives,  
 30 Esters of unsubstituted and substituted benzoic acids, such as  
 4-tert-butylphenyl salicylate, phenyl salicylate, octylphenyl  
 salicylate, dibenzoylresorcinol,  
 bis(4-tert-butylbenzoyl)resorcinol, benzoylresorcinol,  
 2,4-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate,  
 35 hexadecyl-3,5-di-tert-butyl-4-hydroxybenzoate,  
 octadecyl-3,5-di-tert-butyl-4-hydroxybenzoate and  
 2-methyl-4,6-di-tert-butylphenyl-3,5-di-tert-butyl-4-hydroxy-  
 benzoate,  
 40 Acrylates, such as ethyl α-cyano-β,β-diphenylacrylate, isooctyl  
 α-cyano-β,β-diphenylacrylate, methyl α-methoxycarbonylcinnamate,  
 methyl α-cyano-β-methyl-p-methoxycinnamate, butyl-α-cyano-β-  
 methyl-p-methoxycinnamate and  
 methyl-α-methoxycarbonyl-p-methoxycinnamate,  
 45

- sterically hindered amines, such as  
 bis(2,2,6,6-tetramethylpiperidin-4-yl) sebacate,  
 bis(2,2,6,6-tetramethylpiperidin-4-yl) succinate,  
 bis(1,2,2,6,6-pentamethylpiperidin-4-yl) sebacate,  
 5 bis(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate,  
 bis(1,2,2,6,6-pentamethylpiperidin-4-yl)-n-butyl-3,5-di-tert-  
 butyl-4-hydroxybenzylmalonate, the condensation product of  
 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and  
 succinic acid, the condensation product of  
 10 N,N'-bis(2,2,6,6-tetramethylpiperidin-4-yl)hexamethylenediamine  
 and 4-tert-octylamino-2,6-dichloro-1,3,5-triazine,  
 tris(2,2,6,6-tetramethylpiperidin-4-yl) nitrilotriacetate,  
 tetrakis(2,2,6,6-tetramethylpiperidin-4-yl)  
 1,2,3,4-butanetetracarboxylate,  
 15 1,1'-(1,2-ethylene)bis(3,3,5,5-tetramethylpiperazinone),  
 4-benzoyl-2,2,6,6-tetramethylpiperidine,  
 4-stearyloxy-2,2,6,6-tetramethylpiperidine,  
 bis(1,2,2,6,6-pentamethylpiperidin-4-yl)  
 2-n-butyl-2-(2-hydroxy-3,5-di-tert-butylbenzyl)malonate,  
 20 3-n-octyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-  
 dione, bis(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl)  
 sebacate, bis(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl)  
 succinate, the condensation product of  
 N,N'-bis(2,2,6,6-tetramethylpiperidin-4-yl)hexamethylenediamine  
 25 and 4-morpholino-2,6-dichloro-1,3,5-triazine, the condensation  
 product of  
 2-chloro-4,6-bis(4-n-butylamino-2,2,6,6-tetramethylpiperidin-4-  
 yl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, the  
 condensation product of  
 30 2-chloro-4,6-di(4-n-butylamino-1,2,2,6,6-pentamethylpiperidin-4-  
 yl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane,  
 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]-  
 decane-2,4-dione,  
 3-dodecyl-1-(2,2,6,6-tetramethylpiperidin-4-yl)pyrrolidine-2,5-  
 35 dione,  
 3-dodecyl-1-(1,2,2,6,6-pentamethylpiperidin-4-yl)pyrrolidine-2,5-  
 dione, a mixture of 4-hexadecyloxy- and  
 4-stearyloxy-2,2,6,6-tetramethylpiperidine, the condensation  
 product of  
 40 N,N'-bis(2,2,6,6-tetramethylpiperidin-4-yl)hexamethylenediamine  
 and 4-cyclohexylamino-2,6-dichloro-1,3,5-triazine, the  
 condensation product of 1,2-bis(3-aminopropylamino)ethane and  
 2,4,6-trichloro-1,3,5-triazine,  
 4-butylamino-2,2,6,6-tetramethylpiperidine,  
 45 N-(2,2,6,6-tetramethylpiperidin-4-yl)-n-dodecylsuccinimide,  
 N-(1,2,2,6,6-pentamethylpiperidin-4-yl)-n-dodecylsuccinimide,  
 2-undecyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxo-spiro[4.5]-

## 41

- decane, the condensation product of  
 7,7,9,9-tetramethyl-2-cycloundecyl-1-oxa-3,8-diaza-4-oxospiro-  
 [4.5]decane and epichlorohydrin, the condensation products of  
 4-amino-2,2,6,6-tetramethylpiperidine with  
 5 tetramethylolacetylenediureas and  
 poly(methoxypropyl-3-oxy)-[4(2,2,6,6-tetramethyl)piperidinyl]-  
 siloxane,
- Oxalamides, such as 4,4'-dioctyloxyoxanilide,  
 10 2,2'-diethoxyoxanilide,  
 2,2'-dioctyloxy-5,5'-di-tert-butoxanilide,  
 2,2'-didodecyloxy-5,5'-di-tert-butoxanilide,  
 2-ethoxy-2'-ethyloxanilide,  
 N,N'-bis(3-dimethylaminopropyl)oxalamide,  
 15 2-ethoxy-5-tert-butyl-2'-ethoxanilide and its mixture with  
 2-ethoxy-2'-ethyl-5,4'-di-tert-butoxanilide, and mixtures of  
 ortho-, para-methoxy-disubstituted oxanilides and mixtures of  
 ortho- and para-ethoxy-disubstituted oxanilides, and
- 20 2-(2-hydroxyphenyl)-1,3,5-triazines, such as  
 2,4,6-tris-(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine,  
 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-  
 triazine,  
 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-  
 25 triazine,  
 2,4-bis(2-hydroxy-4-propyloxyphenyl)-6-(2,4-dimethylphenyl)-  
 1,3,5-triazine,  
 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-  
 triazine,  
 30 2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,  
 5-triazine,  
 2-(2-hydroxy-4-tridecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-  
 1,3,5-triazine,  
 2-[2-hydroxy-4-(2-hydroxy-3-butyloxypropoxy)phenyl]-4,6-bis(2,4-  
 35 dimethyl)-1,3,5-triazine,  
 2-[2-hydroxy-4-(2-hydroxy-3-octyloxypropoxy)phenyl]-4,6-bis(2,4-  
 dimethyl)-1,3,5-triazine,  
 2-[4-(dodecyloxy/tridecyloxy-2-hydroxypropoxy)-2-hydroxyphenyl]-  
 4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine,  
 40 2-[2-hydroxy-4-(2-hydroxy-3-dodecyloxypropoxy)phenyl]-4,6-bis-(2,  
 4-dimethylphenyl)-1,3,5-triazine,  
 2-(2-hydroxy-4-hexyloxyphenyl)-4,6-diphenyl-1,3,5-triazine,  
 2-(2-hydroxy-4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine,  
 2,4,6-tris[2-hydroxy-4-(3-butoxy-2-hydroxypropoxy)phenyl]-1,3,5-  
 45 triazine and  
 2-(2-hydroxyphenyl)-4-(4-methoxyphenyl)-6-phenyl-1,3,5-triazine.

42

In the context of the present invention, the use of the liquid-crystalline composition according to the invention and its preferred embodiments as a printing ink is claimed. Preferred methods are screen printing, planographic printing and  
5 letterpress printing.

Amongst screen printing methods, particular mention may be made of silk screen printing, frame printing, film printing and textile screen printing, a planographic printing method which may  
10 be mentioned is in particular offset printing, and letterpress printing methods which may be mentioned are in particular flexographic and book printing.

The present invention furthermore relates to the use of the  
15 liquid-crystalline composition according to the invention and its preferred embodiments for printing or coating substrates.

The latter can be articles from a wide variety of areas, for example the automotive and automotive accessory sector, the  
20 leisure, sports and games sector, the cosmetics sector, the textile, leather and jewelry sectors, decorations sector, the gift sector, the writing utensil sector, the packaging sector, the construction and domestic sector, the print products sector, and the medical sector.

25 Examples of such substrates/articles which may be mentioned here are cardboard boxes, packaging, textile and plastic carrier bags, paper, labels, plastic films, vehicles of all types, for example children's vehicles, bicycles, motorcycles, automobiles and  
30 trucks, passenger and cargo aircraft and corresponding vehicle/aircraft and vehicle/aircraft accessories, consumer electronic and data processing equipment, in particular casings of such equipment, roller skates, in-line skates, skis, (wind) surfboards, hang-gliders, medical equipment and spectacle frames.

35 In the context of the present invention, the use of the liquid-crystalline composition according to the invention and its preferred embodiments in electro-optical components is furthermore claimed. In this case, for example, low-crosslinking  
40 or low-crosslinked positions according to the invention can serve as liquid-crystalline matrices, for example in liquid-crystalline displays and screens. In addition, the compositions according to the invention are also suitable as alignment layers in such displays and screens.

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In the context of the present invention, the use of the liquid-crystalline composition according to the invention and its preferred embodiments for counterfeiting-proof marking of articles is furthermore claimed.

5

These articles are, for example, bank notes, stock certificates and other gratuities, check or credit cards, identity cards, but also packaging of expensive food and tobacco, entry tickets, vouchers and luxury products or such luxury products themselves.

10 The keyword regarding the latter is the prevention or at least impediment of trademark piracy.

In the context of the present invention, the use of the liquid-crystalline composition according to the invention and its  
15 preferred embodiments for the production of films or coatings which selectively reflect light in the wavelength range from 250 to 1300 nm is furthermore claimed. Besides (selective) reflection in the visible region of the spectrum, mention may also be made here of reflection of infra-red and ultra-violet light. This can  
20 serve, for example, to protect the substrates provided with such films or coatings against heat or UV radiation.

The present invention furthermore relates to polymers or polymerized films obtained by polymerization of the  
25 liquid-crystalline composition according to the invention and its preferred embodiments.

Furthermore, the use of these polymerized films obtained in this way as optical filters, in particular polarizing colored filters  
30 and notch filters, i.e. narrow-band interference filters, as polarizers, in particular for liquid-crystal displays and screens, as decorations, in particular for lamination purposes, as counterfeiting-proof markings, in particular for check, credit and identity cards, and as reflection media for the selective  
35 reflection of radiation in the wavelength range from 250 to 1300 nm.

The present invention also relates to a process for printing or coating a substrate, which comprises

40

i) applying a liquid-crystalline composition according to the invention and its preferred embodiments to the substrate, and, if appropriate, aligning the liquid-crystalline composition on the substrate,

45

44

- ii) if desired, applying at least one further non-liquid-crystalline print or at least one further non-liquid-crystalline layer

5 or carrying out steps i) and ii) in the reverse sequence,

- iii) if desired, applying at least one absorption layer and/or protective layer and/or optionally thermally activatable adhesive layer, and

10

- iv) curing the prints and/or layers produced in steps i) and, if carried out, ii) and/or iii), where the curing can take place either directly after application of each individual print or each individual layer in step i) and, if carried out, ii) and/or iii) or simultaneously.

15

The present invention furthermore relates to an analogous process to the abovementioned for printing or coating substrates which are at least partially transparent in the wavelength range from 20 250 to 1300 nm.

For simplification, such printed or coated substrates produced by this process are referred to below as multilayer structures. In addition, the process according to the invention should not be 25 taken to mean just that only prints or only layers are applied in all steps i) and, if used, ii), but instead prints and layers can also be applied to the substrates alternately or in any desired sequence and number.

30 The first-mentioned process relates in particular to the production of multilayer structures whose properties are evident when viewed from the top, and the last-mentioned process relates to the production of multilayer structures whose properties are evident when viewed from the top or when viewed through, i.e. the 35 corresponding substrates are at least partially transparent in the wavelength range from 250 to 1300 nm.

As already mentioned above, either firstly a corresponding liquid-crystalline composition can be applied to the substrate 40 and then, if desired, at least one further non-liquid-crystalline print or at least one further non-liquid-crystalline layer can be applied, or the latter can be applied first to the substrate and then coated or printed with the liquid-crystalline composition(s).

45

## 45

If, for example, the multilayer structure produced in accordance with the invention is to be used as a lamination film, the (at least partially light-transparent) substrate of the multilayer structure itself forms the outermost layer in the laminated product, and the application of a protective layer (step iii)) is not absolutely necessary.

However, the multilayer structure may also be of such a design that a release layer is applied between the substrate, which is at least partially transparent in the wavelength range from 250 to 1300 nm, and the liquid-crystalline composition; this release layer, after the multilayer structure has been applied to a further substrate via the side facing away from the substrate, enables detachment of the first substrate (now the outer substrate). This can be achieved, for example, in a hot embossing process.

A suitable adjustment of the adhesion properties of the liquid-crystalline composition on the (first) substrate may make application of a release layer unnecessary. The (first) substrate can in this case be removed directly after application to the further substrate.

If the multilayer structure comprises a colored liquid-crystalline composition, an absorption layer can be applied in order to reinforce or vary the shade. If this multilayer structure is used, for example, as lamination means for dark-colored articles, not only is application of a protective layer, but also of a corresponding absorption layer (step iii)) unnecessary.

The curing can be carried out directly after each application as described in steps i) and, if used, ii) and/or iii) or - if mixing of the prints/layers can be prevented by suitable measures, for example partial/full drying or through different miscibilities and/or viscosities of the printing inks/coating compositions - alternatively simultaneously, i.e. in a curing step (step iii)).

The substrates to be printed or coated may be precoated in one or more colors.

Furthermore, the adhesion properties and/or wetting properties and/or alignment properties of the substrates can, if necessary, be improved by suitable pretreatment.

46

The adhesion properties can be improved, for example, using adhesion promoters, which have already been listed by way of example under the additives in group c7) (priming of the substrates).

5

The wetting properties can be improved, for example, using substrate wetting auxiliaries, by means of which the substrate can be appropriately pretreated and which have already been listed by way of example under the additives in group c4).

10

In addition, the adhesion and wetting properties of the substrates can also be improved by any type of physical/chemical activation. In this connection, particular mention should be made of activation of substrate surfaces by a wide variety of gas plasmas.

An improvement in the alignment properties of the substrates vis à vis the liquid-crystalline compositions according to the invention and their preferred embodiments (in the case where step i) is carried out first) can be achieved, for example, by mechanical or chemical modification of the substrate surface, for example by stretching, polishing, partial dissolution, etching or plasma treatment.

25 Such procedures for modifying the surface properties of substrates are normally known to the person skilled in the art.

Furthermore, the process according to the invention can also be used for printing or coating substrates which are magnetic, electroconductive, photochromic, thermochromic or luminescent or have a combination of these properties.

In this case, the substrates can have said properties per se (bulk properties). However, these properties can also be imparted by admixing (for example doping) corresponding substances (for example magnetic, electroconductive, photochromic, thermochromic or luminescent pigments or photochromic, thermochromic or luminescent dyes) or by coating, printing or vapor-deposition using corresponding printing inks, coating compositions or vapor-deposition compositions.

In addition, combinations are also suitable, allowing, for example, a fluorescent plastic film (for example mass-colored by means of fluorescent dyes or pigments) additionally to be printed with a magnetic or electroconductive printing ink or paste or vapor-deposition-coated with a metal layer.



## 47

If the substrates are precoated in one or more colors, their adhesion properties and/or wetting properties and/or alignment properties have been improved by suitable pretreatment or they have been provided with magnetic, electroconductive,

- 5 photochromic, thermochromic and/or luminescent properties by coating, printing or vapor deposition, these pretreatments are taken to be part of the substrate and not in the sense of step ii) - if this is carried out before step i).

- 10 The application of the prints or layers which takes place, if desired, in step ii) is carried out by means of printing inks or coating compositions by the relevant procedures. These printing inks or coating compositions are based on common binders and solvents and usually also contain (effect) dyes and/or pigments, 15 for example the substances from groups d1) and d2) already mentioned above.

- In accordance with step iii), absorption and/or protective layers can also be applied if desired. This is likewise carried out by 20 means of corresponding coating compositions by the relevant procedures. These coating compositions are again based on conventional binders and solvents and generally contain absorbent dyes and/or pigments and usually also additives which give these absorption and/or protective layers increased scratch resistance, 25 for example (see, for example, the additives from group c8) already mentioned above) or counter light-, heat- and/or oxidation-induced degradation of these layers (for example the additives in the component E) likewise already mentioned above).

- 30 Particularly advantageous multilayer structures, for example with respect to the provision of counterfeiting-proof markings, can be produced by, in step i), applying colored and photochemically polymerizable liquid-crystalline composition according to the invention to substrates (for example plastic films made from 35 polyethylene terephthalate), polymerizing the compositions by means of UV light, then, in step ii), applying further prints or layers containing, for example, IR- or UV-absorbent or fluorescent dyes or pigments, and (if necessary after curing these prints or layers) applying a final absorption layer.

- 40 It should merely be mentioned here that printing methods which can be used for the liquid-crystalline composition and other non-liquid-crystalline layers are - besides conventional coating methods - naturally also full-tone printing methods, such as 45 flexographic, screen or offset printing.

## 48

In daylight, viewed from the film side, such multilayer structures only exhibit a single color impression, which is dependent on the viewing angle. Only using an IR or UV lamp and possibly appropriate viewing equipment (for example IR camera) does the additional identification hidden in the multilayer structures become visible.

The present invention furthermore relates to substrates to which the liquid-crystalline composition according to the invention and its preferred embodiments or polymers or polymerized films obtained therefrom have been applied or which have been coated by the processes according to the invention.

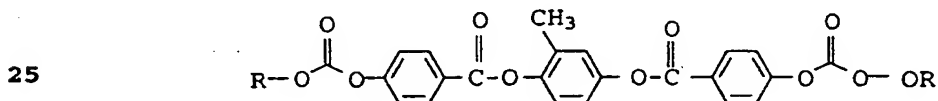
Examples:

15

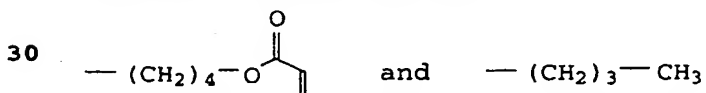
As starting materials for component A) of the liquid-crystalline compositions according to the invention, liquid-crystalline mixtures and a chiral compound as dopant were prepared.

20 Mixture 1 (M1):

A random mixture of the four possible compounds



in which R is the radicals

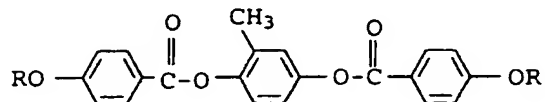


in a random distribution, was prepared in accordance with Example 48 of the specification WO 97/00600 by reacting 1,4-bis[4'-hydroxybenzoyloxy]-2-methylbenzene with a mixture of

35 4-acryloyloxybutoxy chloroformate and butoxy chloroformate (molar ratio 1:1).

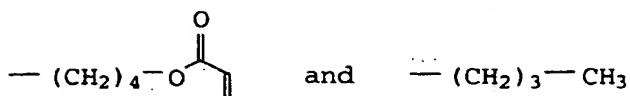
Mixture 2 (M2):

40 A random mixture of the four possible compounds



45 in which R is likewise the radicals

49



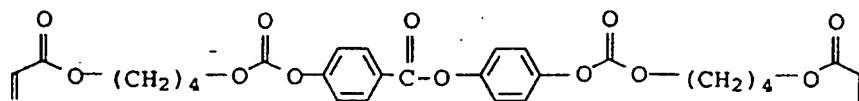
in a random distribution, was prepared in accordance with Example 5 28 of the specification WO 98/47979 by reacting 1,4-bis[4'-hydroxybenzoyloxy]-2-methylbenzene with a mixture of 4-acryloyloxybutyl chloride and butyl chloride (molar ratio 1:1).

Mixture 3 (M3):

10

A mixture was prepared from 62.5% by weight of mixture M1 and 37.5% by weight of the compound

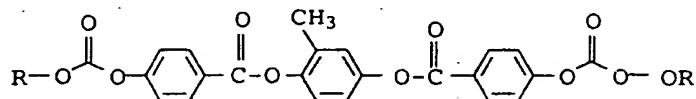
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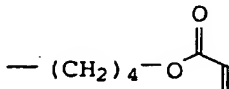
prepared in accordance with Example 18 of the specification  
20 WO 97/00600 by reacting 4-(4'-hydroxybenzoyloxy)phenol with 4-acryloyloxybutyl chloroformate.

Compound 1 (C1):

25 The compounds



30 in which R is the radical



was prepared in accordance with Example 6 of the specification  
35 WO 97/00600 by reacting 1,4-bis[4'-hydroxybenzoyloxy]-2-methylbenzene with 4-acryloyloxybutyl chloroformate.

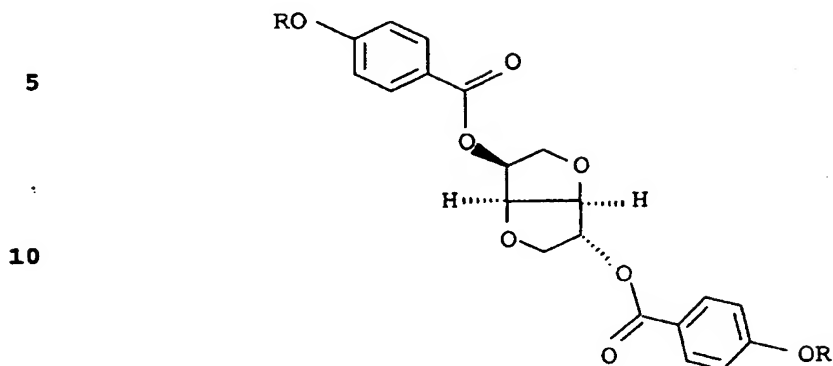
Chiral Compound 1 (CC1):

40

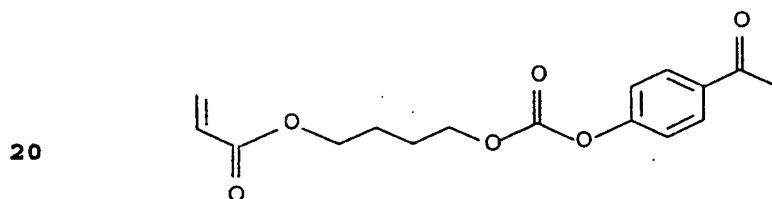
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50

The chiral compound



15 in which R is the radical



was prepared in accordance with Example 1 of the earlier German Patent application 198 43 724.2 by reacting bis[4'-hydroxy-  
25 benzoyl]-1,4:3,6-dianhydrosorbitol with  
4-acryloyloxybutoxycarbonyloxybenzoyl chloride.

Liquid-crystalline compositions (abbreviated to LCC in the tables) were prepared from components A), if desired B) and if  
30 desired C). In the tables below, the percentages are percentages by weight and the ratios are ratios by weight.

Component B):

35 The photoinitiators (b1)) used were Irgacure® 184, 369 or 907, the reactive thinners (b2)) used were hexanediol diacrylate (Laromer® HDDA, BASF Aktiengesellschaft) or ethoxyethoxyethyl acrylate, and the diluents (b3)) used were Solvesso® 100/L33 or xylene.

40

Component C):

The antifoams/deaerators (c1)) used were BYK® 57 or TEGO® Airex 900, and the lubricant and flow auxiliary (c2)) used was BYK®  
45 361.

## 51

Table 1

LCC	Component A)	Component B)	Component C)	Viscosity
	M1	-	-	29.9 Pas
5	1	15% Laromer <sup>®</sup> HDDA	-	not measured
	2	15% Laromer <sup>®</sup> HDDA	1% TEGO <sup>®</sup> Airex 900	~ 3 Pa·s
	3	3% Irgacure <sup>®</sup> 907	1% TEGO <sup>®</sup> Airex 900	~39 Pa·s
10	4	15% Laromer <sup>®</sup> HDDA, 3% Irgacure <sup>®</sup> 907	1% TEGO <sup>®</sup> Airex 900	~ 4 Pa·s
	5	20% Laromer <sup>®</sup> HDDA, 3% Irgacure <sup>®</sup> 907	1% TEGO <sup>®</sup> Airex 900	~ 2 Pa·s
15	6	15% Laromer <sup>®</sup> HDDA	1.2% BYK <sup>®</sup> 361	~ 3 Pa·s
	7	3% Irgacure <sup>®</sup> 907	1.2% BYK <sup>®</sup> 361	~39 Pa·s
20	8	15% Laromer <sup>®</sup> HDDA, 3% Irgacure <sup>®</sup> 907	1.2% BYK <sup>®</sup> 361	~ 4 Pa·s
25	9	20% Laromer <sup>®</sup> HDDA, 3% Irgacure <sup>®</sup> 907	1.2% BYK <sup>®</sup> 361	~ 2 Pa·s

30 Compositions 1, 2, 4, 6, 8 and in particular 5 and 9 caused no problems in screen printing.

Table 2

LCC	Component A)	Component B)	Component C)	Viscosity
35	M2	-	-	9.6 Pa·s
	10	-	-	~ 9 Pa·s
	11	15% Laromer <sup>®</sup> HDDA	1% TEGO <sup>®</sup> Airex 900	~ 2 Pa·s

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Table 2 (continuation)

LCC	Component A)	Component B)	Component C)	Viscosity
5 12	M2:CC1 (97:3) 81%	15% Laromer <sup>®</sup> HDDA, 3% Irgacure <sup>®</sup> 907	1% TEGO <sup>®</sup> Airex 900	~ 2 Pa.s
13	M2:CC1 (97:3) 83.8%	15% Laromer <sup>®</sup> HDDA	1.2% BYK <sup>®</sup> 361	~ 2 Pa.s
10 14	M2:CC1 (97:3) 80.8%	15% Laromer <sup>®</sup> HDDA, 3% Irgacure <sup>®</sup> 907	1.2% BYK <sup>®</sup> 361	~ 2 Pa.s

15 Compositions 10, 11, 13 and in particular 12 and 14 cause no problems in the screen printing.

Table 3

LCC	Component A)	Component B)	Component C)	Viscosity
20 15	V1:CC1 (97:3)	-	-	not measured
16	SG 15 96.95%	3% Irgacure <sup>®</sup> 907	0.05% BYK <sup>®</sup> 361	not measured

25 Composition 16 causes no problems in screen printing.

Table 4

LCC	Component A)	Component B)	Component C)	Viscosity
30 17	M3:CC1 (96.5:3.5) 90%	9% Laromer <sup>®</sup> HDDA	1% Tego <sup>®</sup> Airex 900	4.1 Pa.s
18	M3:CC1 (96.5:3.5) 96%	3% Irgacure <sup>®</sup> 369	1% Tego <sup>®</sup> Airex 900	11.5 Pa.s
35 19	M3:CC1 (96.5:3.5) 87%	9% Laromer <sup>®</sup> HDDA 3% Irgacure <sup>®</sup> 369	1% Tego <sup>®</sup> Airex 900	4.4 Pa.s
40 20	M3:CC1 (96.5:3.5) 87%	9% Laromer <sup>®</sup> HDDA 3% Irgacure <sup>®</sup> 184	1% Tego <sup>®</sup> Airex 900	3.8 Pa.s
45 21	M3:CC1 (95:5) 87%	9% Laromer <sup>®</sup> HDDA 3% Irgacure <sup>®</sup> 369	1% Tego <sup>®</sup> Airex 900	4.5 Pa.s

Table 4 (Continuation)

LCC	Component A)	Component B)	Component C)	Viscosity
5 22	M3:CC1 (95:5) 87%	9% ethoxy- ethoxy ethyl- acrylate 3% Irgacu- re <sup>®</sup> 369	1% Byk <sup>®</sup> 57	4.3 Pa·s
10 23	M3:CC1 (96:4) 85.5%	10% Laromer <sup>®</sup> HDDA 3% Irgacu- re <sup>®</sup> 369	1.5 % Tego <sup>®</sup> Airex 900	2.8 Pa·s
15 24	M3:CC1 (97:3) 85.5%	10% Laromer <sup>®</sup> HDDA 3% Irgacu- re <sup>®</sup> 369	1.5 % Tego <sup>®</sup> Airex 900	2.5 Pa·s
20 25	M3:CC1 (97:3) 84%	9% Laromer <sup>®</sup> HDDA 3% Irgacu- re <sup>®</sup> 369 3 % xylene	1% Tego <sup>®</sup> Airex 900	1.8 Pa·s
25 26	M3:CC1 (97:3) 83.5%	9% Laromer <sup>®</sup> HDDA 3% Irgacu- re <sup>®</sup> 369 3% Solves- so <sup>®</sup> 100/L33	1,5 % Tego <sup>®</sup> Airex 900	2.0 Pa·s
30 27	M3:CC1 (96:4) 83.5%	9% Laromer <sup>®</sup> HDDA 3% Irgacu- re <sup>®</sup> 369 4 % xylene	1.5 % Tego <sup>®</sup> Airex 900	1.5 Pa·s

Compositions 17 and 19 to 27 cause no problems in screen printing and the liquid-crystalline composition aligns well. Film formation by the prints was good, and the color change was very clearly pronounced.

Print/coating examples:

In all the examples below, the substrate used was polyethyleneterephthalate film (12  $\mu$ m thick, Teijin) which had been coated with Composition 16 according to the invention from Table 3 by the method described in the earlier German Patent Application 197 38 369.6 using tetrahydrofuran as diluent.

## 54

## Preparation of Base Mixture 1 (BM 1):

35% by weight of methoxypropyl acetate, 35% by weight of butyl glycol, 20% by weight of white spirit and 10% by weight of Laroflex<sup>®</sup> MP45 (wetting agent based on PVC, BASF Aktiengesellschaft) were mixed.

## Preparation of Base Mixture 2 (BM 2):

55% by weight of butyl glycol, 25% by weight of Laroflex<sup>®</sup> MP45 (BASF Aktiengesellschaft), 15% by weight of n-hexyl diglycol and 5% by weight of methoxypropyl acetate were mixed. 0.2% by weight of Uvinul<sup>®</sup> 3039 (light/oxidation stabilizer, BASF Aktiengesellschaft), based on this mixture, was added.

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## Example 1:

A mixture of 20% by weight of Ultraphor<sup>®</sup> SF MO (a UV-excitabile optical brightener) and 80% by weight of BM 1 were diluted with BM 2 in a weight ratio of 1:39 to an Ultraphor<sup>®</sup> SF MO content of 0.5% by weight in the mixture as a whole. Using the resultant printing ink, a picture was printed onto the side of the plastic film coated with the liquid-crystalline composition by flat-bed screen printing using a fine screen (180 T). After drying, a black full-tone screen print was printed over this picture using a larger screen mesh (120 T).

The black printing ink used for this purpose was prepared by dispersing 20% by weight of carbon black (CK3, Degussa) in 80% by weight of BM 1 and diluting the mixture with BM 2 in a weight ratio of 1:1 to give a carbon black content of 10% by weight in the mixture as a whole.

The colored nature of the liquid-crystalline (cholesteric) layer is emphasized by the coating with the black printing ink. The viewer cannot see the picture hidden in the multilayer structure either in incident light or in transmitted light. However, the picture becomes visible on illumination with a UV lamp (Camag, emitted wavelength 366 nm).

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## Example 2:

A dispersion of 20% by weight of carbon black (CK3, Degussa) and 80% by weight of BM 1 was diluted with BM 2 in a weight ratio of 1:9 to give a carbon black content of 2% by weight in the mixture as a whole. Using this printing ink, a picture was printed on the side of the plastic film coated with the liquid-crystalline



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composition by means of flat-bed screen printing using a fine screen (180 T). After drying, a black full-tone screen print was printed on top of this picture using a larger screen mesh (120 T).

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The black printing ink used for this purpose was prepared by dispersing 20% by weight of Paliogen Black L 0086 (BASF Aktiengesellschaft) in 80% by weight BM 1 and diluting the mixture with BM2 in a weight ratio of 1:1 to give a Paliogen Black L 0086 content of 10% by weight in the mixture as a whole.

The viewer sees only the color effect of the liquid-crystalline (cholesteric) layer and a black full-tone print. Using IR photography (EMO Elektronik GmbH), only the picture is visible, while the black full-tone print is not reflected.

## Example 3:

A dispersion of 7.5% by weight of Ultraphor® SF MO and 7.5% by weight of carbon black (CK3) and 85% by weight of BM 1 was diluted with BM 2 in a weight ratio of 1:9 to give an Ultraphor® SF MO and carbon black (CK3) content of 0.75% by weight each in the mixture as a whole. Using this printing ink, a picture was printed on the side of the plastic film coated with the liquid-crystalline composition by means of flat-bed screen printing using a fine screen (180 T). After drying, a black full-tone screen print was printed on top of this picture using a larger screen mesh (120 T).

The black printing ink used for this purpose was prepared as described in Example 2.

The colored nature of the liquid-crystalline (cholesteric) layer is emphasized by the coating with the black printing ink. The viewer cannot see the picture hidden in the multilayer structure either in incident light or in transmitted light. However, the picture becomes visible both on illumination with a UV lamp and by IR photography.

It is of course also possible to apply different (for example complementary) UV and IR pictures in separate prints/layers.

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We claim:

1. A liquid-crystalline mixture comprising, as components,

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A) a liquid-crystalline mixture comprising at least one compound selected from the group consisting of the compounds of the formula Ia

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$Z^1-Y^1-A^1-Y^3-M^1-Y^4-A^2-Y^2-Z^2$  Ia

and of the formula Ib

$Z^3-Y^5-A^3-Y^7-M^2-P$  Ib,

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where the variables, independently of one another, have the following meanings:

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P is hydrogen,  $C_1$ - $C_{15}$ -alkyl, which may be monosubstituted or polysubstituted by methyl, fluorine, chlorine or bromine and in which non-adjacent  $CH_2$ -groups may be replaced by oxygen, sulfur,  $-CO-$ ,  $-O-CO-$ ,  $-CO-O-$  or  $-O-CO-O-$ , or a  $-Y^8-A^4-Y^6-Z^4$  group, where the variables are as defined above,

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$Z^1$  to  $Z^4$  are polymerizable groups,

30

$Y^1$  to  $Y^8$  are each a single chemical bond, oxygen, sulfur,  $-O-CO-$ ,  $-CO-O-$ ,  $-O-CO-O-$ ,  $-CO-NR-$ ,  $-NR-CO-$ ,  $-O-CO-NR-$ ,  $-NR-CO-O-$  or  $-NR-CO-NR-$ ,

R is hydrogen or  $C_1$ - $C_4$ -alkyl,

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$A^1$  to  $A^4$  are spacers having 1 to 30 carbon atoms, in which the carbon chain may be monosubstituted or polysubstituted by methyl, fluorine, chlorine or bromine and/or interrupted by ether oxygen, thioether sulfur or by non-adjacent imino or  $C_1$ - $C_4$ -alkylimino groups,

40

$M^1$  is a mesogenic group of the formula Ic

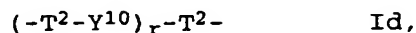
$-T^1-Y^9-T^1'-$  Ic,

45

and

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M<sup>2</sup> is a mesogenic group of the formula Id



5 where the variables in the formulae Ic and Id,  
independently of one another, are as defined below:

T<sup>1</sup>, T<sup>1'</sup> and T<sup>2</sup> are divalent saturated or unsaturated  
carbocyclic or heterocyclic radicals,

10 Y<sup>9</sup> and Y<sup>10</sup> are bridging units as defined for Y<sup>1</sup> to Y<sup>8</sup> or  
-CH<sub>2</sub>-O-, -O-CH<sub>2</sub>-, -CH=N-, -N=CH- or -N=N-,

r is a value of 0, 1, 2 or 3,

15 where the radicals T<sup>2</sup> and Y<sup>10</sup>, in the case where r is not  
0, may be identical or different,

20 B) if desired, further additives selected from the group  
consisting of

b1) photoinitiators,

b2) reactive thinners and

25 b3) diluents,

C) if desired, further additives taken from the group  
consisting of

30 c1) antifoams and deaerators,

c2) lubricants and flow-control agents,

35 c3) thermally curing or radiation-curing auxiliaries,

c4) substrate wetting auxiliaries,

c5) wetting and dispersion auxiliaries,

40 c6) hydrophobicizing agents,

c7) adhesion promoters and

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c8) auxiliaries for improving the scratch resistance,

D) if desired, further additives selected from the group consisting of

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d1) dyes and

d2) pigments,

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and

E) if desired, further additives selected from the group consisting of light, heat and/or oxidation stabilizers.

15 2. A liquid-crystalline composition as claimed in claim 1, comprising, as component A),

20 a liquid-crystalline mixture comprising at least one compound of the formula Ia

$Z^1-Y^1-A^1-Y^3-M^1-Y^4-A^2-Y^2-Z^2$  Ia

and at least one compound of the formula Ib

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$Z^3-Y^5-A^3-Y^7-M^2-P$  Ib,

where the variables are as defined in claim 1.

30 3. A liquid-crystalline composition as claimed in claim 1 or 2, comprising, as further additives in component B),

b1) at least one photoinitiator,

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b2) at least one reactive thinner containing photopolymerizable groups, and, if desired,

b3) diluents,

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and, if desired, further additives selected from the group consisting of components C), D) and E).

4. Liquid-crystalline composition as claimed in claim 1 or 2, comprising component C) and, if desired, further additives  
45 selected from the group consisting of components B), D) and E).

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5. Liquid-crystalline composition as claimed in claim 1 or 2, comprising, as component B),
- b1) at least one photoinitiator,
  - b2) at least one reactive thinner containing photopolymerizable groups, and, if desired,
  - b3) diluents,
- component C) and, if desired, further additives selected from the group consisting of components D) and E).
6. Liquid-crystalline composition as claimed in claims 1 to 5, in which the proportion of compounds of the formulae Ia and/or Ib in component A) is from 40 to 99.5% by weight, based on the total amount of component A).
7. Liquid-crystalline composition as claimed in claims 1 to 6, in which Z<sup>1</sup>-Y<sup>1</sup>-, Z<sup>2</sup>-Y<sup>2</sup>-, Z<sup>3</sup>-Y<sup>5</sup>- and, if present, Z<sup>4</sup>-Y<sup>6</sup>- are selected from the group consisting of methacryloyloxy, acryloyloxy and vinyloxy.
8. Liquid-crystalline composition as claimed in claims 1 to 7, having a viscosity of from 0.5 to 10.0 Pa·s at 20°C.
9. The use of a liquid-crystalline composition as claimed in claims 1 to 8 as a printing ink.
10. The use of a liquid-crystalline composition as claimed in claims 1 to 8 for printing or coating substrates.
11. The use of a liquid-crystalline composition as claimed in claims 1 to 8 in electro-optical components.
12. The use of a liquid-crystalline composition as claimed in claims 1 to 8 for counterfeiting-proof marking of articles.
13. The use of a liquid-crystalline composition as claimed in claims 1 to 8 for the production of films or coatings which selectively reflect light in the wavelength range from 250 to 1300 nm.
14. A polymer or polymerized film obtained by polymerizing a liquid-crystalline composition as claimed in claims 1 to 8.
15. The use of a polymerized film as claimed in claim 14 as an

optical filter, polarizer, decoration, counterfeiting-proof marking or reflection medium for the selective reflection of radiation in the wavelength range from 250 to 1300 nm.

5 16. A process for printing or coating a substrate, which comprises

- 10 i) applying a liquid-crystalline composition as claimed in claims 1 to 8 to the substrate, and, if appropriate, aligning the liquid-crystalline composition on the substrate,
- 15 ii) if desired, applying at least one further non-liquid-crystalline print or at least one further non-liquid-crystalline layer,
- or carrying out steps i) and ii) in the reverse sequence,
- 20 iii) if desired, applying at least one absorption layer and/or protective layer and/or optionally thermally activatable adhesive layer, and
- 25 iv) curing the prints and/or layers produced in steps i) and, if carried out, ii) and/or iii), where the curing can take place either directly after application of each individual print or each individual layer in step i) and, if carried out, ii) and/or iii) or simultaneously.

30 17. A process for printing or coating a substrate which is at least partially transparent in the wavelength range from 250 to 1300 nm, which comprises

- 35 i) applying a liquid-crystalline composition as claimed in claims 1 to 8 to the substrate, and, if appropriate, aligning the liquid-crystalline composition on the substrate,
- 40 ii) if desired, applying at least one further non-liquid-crystalline print or at least one further non-liquid-crystalline layer,
- or carrying out steps i) and ii) in the reverse sequence,
- 45 iii) if desired, applying at least one absorption layer and/or protective layer and/or optionally thermally activatable adhesive layer, and

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iv) curing the prints and/or layers produced in steps i) and, if carried out, ii) and/or iii), where the curing can take place either directly after application of each individual print or each individual layer in step i) and, if carried out, ii) and/or iii) or simultaneously.

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18. A substrate to which a liquid-crystalline composition as claimed in claims 1 to 8 or a polymer or polymerized film as claimed in claim 14 has been applied or which has been printed or coated by a process as claimed in claim 16 or 17.

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